

We claim:

1. A process for preparing dye-comprising aqueous polymer
5 dispersions by aqueous emulsion polymerization of
ethylenically unsaturated monomers in the presence of
free-radical initiators, in which process at least some of
the monomers are employed in the form of an oil-in-water
emulsion E1 whose disperse phase comprises at least one
10 oil-soluble dye, wherein the disperse phase of E1 is formed
essentially of dye-comprising monomer droplets having a
diameter < 500 nm.
2. A process as claimed in claim 1, wherein the ethylenically
15 unsaturated monomers comprise at least one monoethylenically
unsaturated monomer A having a water solubility > 0.01 g/l
and at least one monoethylenically unsaturated monomer B
having a water solubility < 0.01 g/l.
- 20 3. A process as claimed in either of the preceding claims,
wherein the oil droplets of the oil-in-water emulsion E1
comprise a noncopolymerizable compound B' having a water
solubility < 0.01 g/l.
- 25 4. A process as claimed in any of the preceding claims, wherein
the ethylenically unsaturated monomers comprise at least one
monomer C which has at least two nonconjugated double bonds.
- 30 5. A process as claimed in any of the preceding claims, wherein
the ethylenically unsaturated monomers comprise at least one
monoethylenically unsaturated monomer D which is different
from the monomers C and has a crosslinking action.
- 35 6. A process as claimed in any of the preceding claims, wherein
the oil-soluble dye is selected from oil-soluble derivatives
of naphthalene, perylene, terrylene, quaterylene,
diketopyrrolopyrrole, from perinone dyes, coumarin dyes,
oxazine dyes, anthracene dyes, azo dyes, anthraquinone dyes,
methine dyes, azamethine dyes, isoindoline dyes and
40 isoindolinone dyes, porphyrins, phthalocyanines and
naphthalocyanines.
7. A process as claimed in any of the preceding claims, wherein
the oil-soluble dye is an optical brightener.

8. A process as claimed in claim 7, wherein the optical brightener is selected from compounds from the classes of the bisstyrylbenzenes, stilbenes, benzoxazoles, coumarins, pyrenes and naphthalenes.

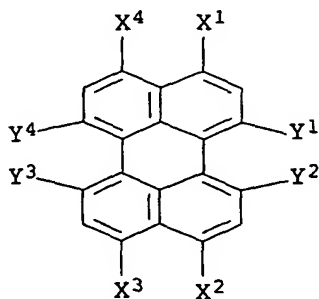
5

9. A process as claimed in any of the preceding claims, wherein the oil-soluble dye has at least one copolymerizable, ethylenically unsaturated double bond which does not belong to the chromophore of the dye.

10

10. A process as claimed in claim 9, wherein the oil-soluble organic dye is selected from perylene dyes of the formula III

15



(III) ,

20

in which one or two of the groups X^1 to X^4 , Y^1 to Y^4 is or are a radical of the formula IV

25



(IV)

in which

30

X is selected from a single bond, ethynylene or $(CH_2)_k-X'$ where $k = 0, 1, 2, 3$ or 4 and X' is selected from $-O-$; $-N(R)-$; $-S-$; $-O-C(O)-$; $-O-C(O)-O-$; $-O-C(O)-N(R')-$; $-N(R')-C(O)-$; $-N(R')-C(O)-O-$; $-N(R')-C(O)-N(R'')-$; $-C(O)-$; $-C(O)-O-$; $-C(O)-N(R')-$; $-S(O)_2-O-$; $-S(O)_2-N(R')-$; $-O-S(O)_2-$; $-N(R')-S(O)_2-$;

35

in which R is hydrogen, linear or branched C_1-C_6 -alkyl, aryl, aryl- C_1-C_6 -alkyl, C_1-C_6 -alkylcarbonyl, arylcarbonyl or formyl and R' , R'' independently of one another are hydrogen, linear or branched C_1-C_6 -alkyl, aryl or aryl- C_1-C_6 -alkyl which are optionally substituted by OH, halogen, C_1-C_4 -alkyl or C_1-C_4 -alkyloxy,

40

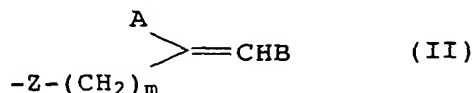
S is selected from a single bond, C_1-C_{12} -alkylene which can be interrupted by one or more nonadjacent oxygen atoms, sulfur atoms or (alkyl)imino groups, or is 1,2-, 1,3- or

45

1,4-phenylene which optionally has one or two substituents selected from C₁-C₄-alkyl, C₁-C₄-alkyloxy or halogen, or is 1,2-, 1,3- or 1,4-xylylene which is optionally substituted as for phenylene, and

5

P is a polymerizable group of the formula II



10

in which

A and B independently of one another are hydrogen, C₁-C₆-alkyl or phenyl, or A and B together with the double bond to which they are attached form a cyclopentene or cyclohexene ring,

15

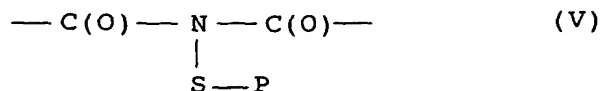
m is 0, 1, 2 or 3, and

20

Z is a single bond or possesses one of the definitions indicated above for X', or

X¹ together with X⁴ and/or X² together with X³ are a group of the formula V

25



30

in which S and P possess one of the above-mentioned definitions, and

the remaining groups X¹ to X⁴, Y¹ to Y⁴ independently of one another are selected from hydrogen, linear or branched C₁-C₁₂-alkyl which can if desired be interrupted by one or more nonadjacent oxygen atoms, sulfur atoms or by (alkyl)imino groups and/or can be substituted by OH and/or halogen, or are cycloalkyl, heterocycloalkyl, aryl, hetaryl, aryl-C₁-C₆-alkyl, hetaryl-C₁-C₆-alkyl, C₂-C₁₈-alkynyl, arylethynyl, tris(C₁-C₄-alkyl)silylethynyl, cyano, nitro, halogen;

35

40

and/or atomic groups selected from:

-O-R; -O-C(O)-R'; -N(R')-C(O)-R''; -NRR'; -C(O)-R; -C(O)-OR'; -C(O)-NR'R''; -N(R')-C(O)-OR; -N(R')C(O)-NR'R'', -O-S(O)₂-R, -N(R')-S(O)₂-R'', in which R, R' and R'' have the definitions indicated above,

45

the remaining groups X^1 together with X^4 and/or X^2 together with X^3 can furthermore be $-X''-C(O)-$, $-C(O)-N(R''')-C(O)-$ or $-C(O)-O-C(O)-$, in which R''' has the definitions indicated for R' and X'' is $-CH=CH-$, 1,2-phenylene, 1,2-naphthylene, 2,3-naphthylene or 2,3-pyridinylene, each of which is unsubstituted or substituted once or twice by C_1-C_4 -alkylene, C_1-C_4 -alkoxy or halogen.

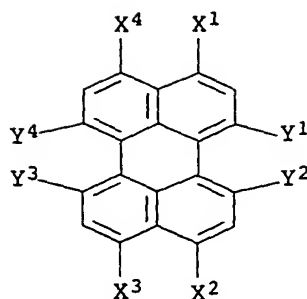
11. A process as claimed in any of the preceding claims, wherein the initiator is soluble in water.
12. A process as claimed in claim 11, wherein the water-soluble initiator comprises a nonionic peroxide, especially hydrogen peroxide, and, if desired, one or more reducing agents.
13. A process as claimed in any of the preceding claims, wherein the dye-comprising monomer droplets of the oil-in-water emulsion E1 have an average diameter \bar{d}_2 in the range from 100 to 400 nm.
14. A process as claimed in any of the preceding claims, wherein the oil-in-water emulsion E1 is prepared by homogenizing a conventional, dye-comprising oil-in-water emulsion of the monomers by means of ultrasound, the dye in the monomer droplets of the conventional emulsion being in dissolved or molecularly disperse form.
15. A dye-comprising aqueous polymer dispersion in which the polymer particles have an average diameter $d_2 < 1000$ nm and comprise at least one oil-soluble dye in molecularly disperse form and which, furthermore, is composed of at least one monoethylenically unsaturated monomer A having a water solubility > 0.01 g/l and at least one further, polymerization-active compound which is selected from
 - monoethylenically unsaturated monomers B having a water solubility < 0.01 g/l,
 - monomers C which have at least two nonconjugated, ethylenically unsaturated double bonds,
 - crosslinking monomers D, and
 - copolymerizable dyes from either of claims 9 and 10.
16. A dye-comprising aqueous polymer dispersion as claimed in claim 15, wherein the polymeric matrix formed from the copolymerized monomers A, B and, if desired, C and D is composed of

- from 50 to 99.5% by weight of monomers A,
- from 0.5 to 50% by weight of monomers B,
- from 0 to 30% by weight of monomers C, and
- from 0 to 30% by weight of monomers D

- 5
17. A dye-comprising aqueous polymer dispersion as claimed in claim 15 or 16, comprising at least one noncopolymerizable dye, wherein the polymer matrix comprises, in copolymerized form, at least one compound selected from the monomers C and
- 10 the compounds D, in amounts of > 0.1% by weight, based on the polymer matrix.
18. A dye-comprising aqueous polymer dispersion as claimed in any of claims 15 to 17, comprising at least one copolymerizable
- 15 dye from either of claims 9 and 10.
19. A dye-comprising aqueous polymer dispersion as claimed in any of claims 15 to 18, wherein the polymer particles have a monomodal particle size distribution with an average particle
- 20 diameter d_z in the range from 100 to 400 nm.
20. A dye-comprising aqueous polymer dispersion as claimed in any of claims 15 to 19, wherein the monomers A copolymerized in the polymer particles comprise
- 25
- from 0.5 to 30% by weight of at least one monomer A1 having a water solubility > 60 g/l (in each case at 25°C and 1 atm), based on the total monomer amount, and
- 30
- from 70 to 99.5% by weight of at least one monomer A2 having a water solubility < 60 g/l (in each case at 25°C and 1 atm), based on the total monomer amount.
21. A dye-comprising aqueous polymer dispersion as claimed in claim 20, wherein the monomers A2 are selected from
- 35 monoethylenically unsaturated cationic monomers.
22. A dye-comprising aqueous polymer dispersion as claimed in claim 20, wherein the monomers A2 are selected from
- 40 monoethylenically unsaturated monomers which have at least one acid group, possibly in deprotonated form.
23. A dye-comprising polymer powder obtainable by drying an aqueous polymer dispersion as claimed in any of claims 15 to
- 45 22.

24. An aqueous dye-comprising formulation comprising:
- i. at least one dye-comprising polymer which is present in the formulation in the form of dispersed polymer particles and is selected from the polymers present in the aqueous, dye-comprising-polymer dispersion as claimed in any of claims 14 to 22, and the polymer powder as claimed in claim 23 and
 - ii. customary auxiliaries.
25. A formulation as claimed in claim 24, additionally comprising at least one water-soluble polymer PW.
26. A formulation as claimed in claim 25, wherein the polymer PW has cationic groups.
27. A formulation as claimed in claim 26, wherein the polymer PW is a copolymer which is composed of at least one monoethylenically unsaturated, cationic monomer, especially a monomer having at least one quaternary ammonium or immonium group, and at least one further, neutral monomer.
28. A formulation as claimed in claim 27, wherein the polymer PW is selected from:
- copolymers of 1-vinylpyrrolidone with 1-vinyl-3-alkylimidazolium salts,
 - copolymers of 1-vinylpyrrolidone with methacryloyloxyethyltrialkylammonium salts,
 - terpolymers of vinylpyrrolidone and vinylcaprolactam with 1-vinyl-3-alkylimidazolium salts.
29. A formulation as claimed in claim 25, wherein the polymer PW has acidic functional groups and/or anionic functional groups.
30. A formulation as claimed in claim 29, wherein the polymer PW is a copolymer composed of
- at least one monoethylenically unsaturated monomer MA selected from monomers having at least one acid group and salts thereof, and
 - at least one further, neutral monomer.
31. A formulation as claimed in claim 29 or 30, wherein the polymer PW is selected from

- homopolymers and copolymers of
2-acrylamido-2-methylpropanesulfonic acid,
 - 5 - copolymers of acrylic acid and/or of methacrylic acid
with styrene,
 - copolymers of acrylic acid and/or of methacrylic acid
with C₁-C₁₀-alkyl esters of acrylic acid and/or of
methacrylic acid,
 - 10 - copolymers of maleic acid or of maleic anhydride with
olefins, especially with diisobutene,
 - the formaldehyde condensates of an arylsulfonic acid,
15 especially a naphthalenesulfonic acid
- and salts thereof.
32. The use of an aqueous, dye-comprising formulation as claimed
20 in any of claims 24 to 31 as an ink, especially for the
inkjet process.
33. An aqueous pigmented formulation comprising
- 25 i. at least one dye-comprising polymer which is present in
the formulation in the form of dispersed polymer
particles and is selected from the polymers of the
aqueous dye-comprising polymer dispersion as claimed in
any of claims 15 to 22 and from the polymer powder as
30 claimed in claim 23, and whose oil-soluble dye comprises
at least one optical brightener,
 - ii. at least one dye-free, film-forming water-insoluble
polymer which is composed of ethylenically unsaturated
35 monomers, in the form of its aqueous dispersion,
 - iii. at least one inorganic white pigment alone or together
with an inorganic filler, and
 - 40 iv. auxiliaries.
34. The use of a formulation as claimed in claim 33 as a paper
coating slip.
- 45 35. A perylene dye of the formula III



(III)

10

in which X^1 to X^4 and Y^1 to Y^4 are as defined in claim 10, with the exception of those compounds of the formula III in which

15 X^1 together with X^4 is a group of the formula V as defined in claim 10, and
 X^2 together with X^3 is a group of the formula
 $-C(O)-N(R''')-C(O)-$.

20 36. A perylene dye as claimed in claim 35, of the formula III, in which

X^1 , X^3 and X^4 independently of one another are selected from
 25 hydrogen, linear or branched C_1 - C_{12} -alkyl which can be uninterrupted or interrupted by one or more nonadjacent oxygen atoms, sulfur atoms or by (alkyl)imino groups and/or can be unsubstituted or substituted by OH and/or halogen, and from cycloalkyl, cycloalkyloxy,
 30 C_2 - C_8 -alkynyl, tris(C_1 - C_4 -alkyl)silylethynyl, aryl, aryloxy, halogen and cyano,

X^2 is a group of the formula IV



35

in which X, S and P are as defined in claim 10, and

Y^1 to Y^4 possess the definitions indicated in claim 10 other than $-X-S-P$.

40

37. A perylene dye as claimed in claim 35, in which

X^1 together with X^4 is $-C(O)-N(R''')-C(O)-$ or $-C(O)-O-C(O)-$ in which R''' is as defined in claim 10,

45

X^2 is a group of the formula IV

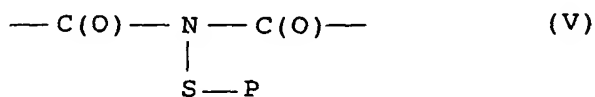


in which X, S and P are as defined in claim 10 and

X³, Y¹ to Y⁴ have the definitions indicated in claim 10 other than X-S-P.

38. A perylene dye as claimed in claim 35, in which

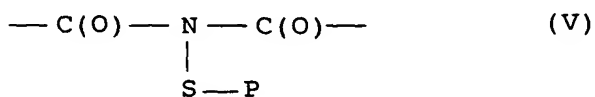
X² together with X³ is a group of the formula V



in which S and P are as defined in claim 10, and

X¹, X⁴ and Y¹ to Y⁴ are as defined in claim 10 other than -X-S-P.

39. A perylene dye as claimed in claim 35, in which X¹ together with X⁴ and X³ together with X² are a group of the formula V



in which S and P are as defined in claim 10 and Y¹ to Y⁴ have the definitions indicated in claim 10 other than -X-S-P.

40. A perylene dye as claimed in any of claims 35 to 39, in which

P in formula (IV) or (V) is vinyl, allyl, methallyl, acrylamido, methacrylamido, acryloxy, methacryloxy, 3-vinylureido, 3-allylureido, 3-methallylureido, N-vinylaminocarbonyloxy, N-allylaminocarbonyloxy or N-methallylaminocarbonyloxy.

135/iT/135